



## Current density - overvoltage relations for solid oxide electrodes

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# CURRENT DENSITY - OVERVOLTAGE RELATIONS FOR SOLID OXIDE ELECTRODES

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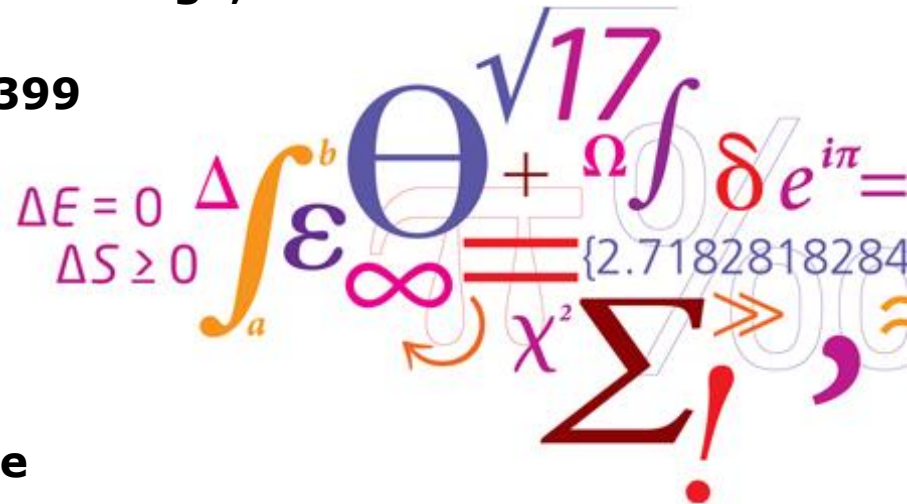
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Smart Energy Conversion and Storage  
IV Polish Forum, October 1 – 4, 2013

DTU Energy Conversion  
Department of Energy Conversion and Storage

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# Outline

- **Motivation**
- **Introduction**
- **Charge transfer limitations - Butler-Volmer or other  $i - V$  relations?**
- **Some experimental findings**
- **Sketching a realistic model type**
- **Concluding remarks**

# Motivation: Energy plan for Denmark

**2020: 50 % electricity from Renewables**

**2035: 0 % fossil energy in power and heat production**

**2050: 100 % renewable energy**

## Challenges

**1) Increasing share of fluctuating production**

**2) Liquid fuels will still be needed; biomass is limited**

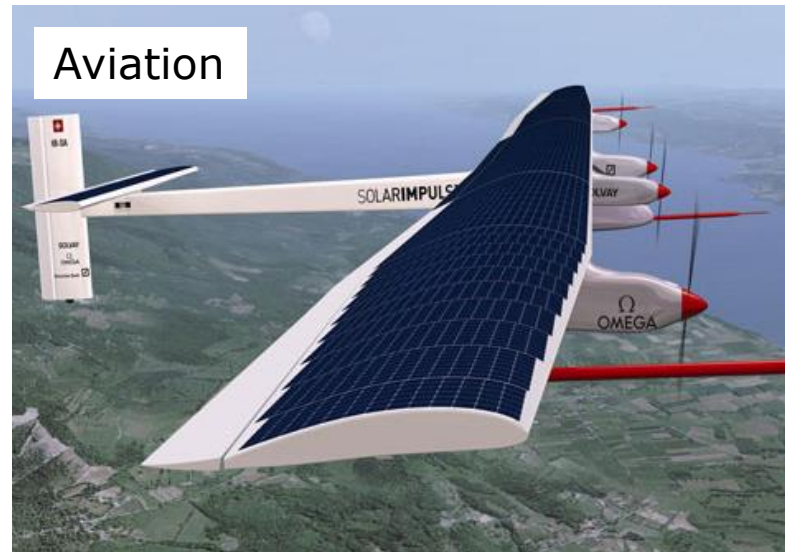
***Solid oxide electrolyzers and fuel cell are needed for conversion of renewable electricity into hydrocarbon fuels and back again***

Heavy transport



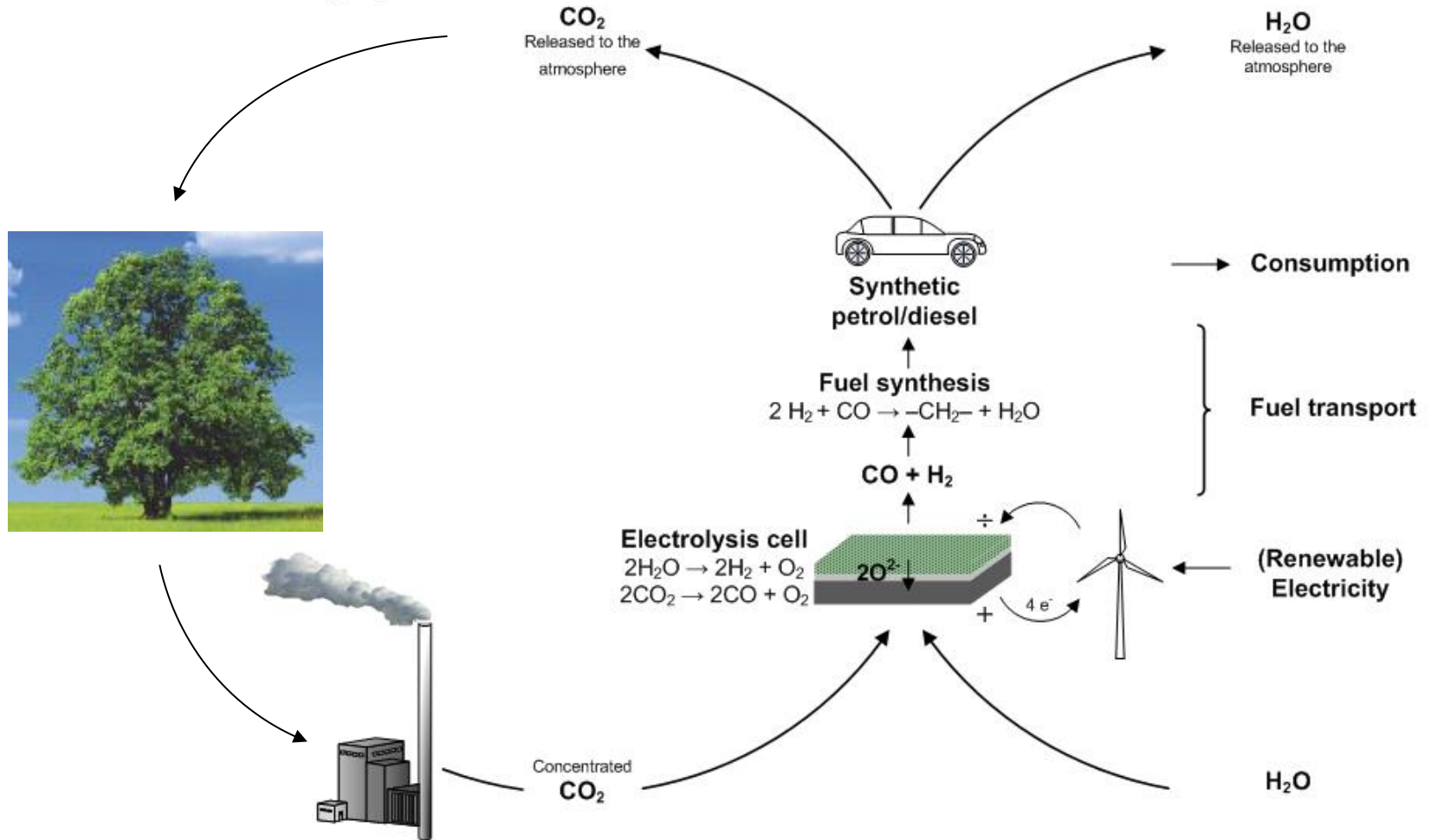
Photo © Dennis Child - ROTRAN

Aviation



# Vision: Biomass + CO<sub>2</sub> recycling

## Short term realisation - CO<sub>2</sub> capture from industrial sources



# Introduction I

## **DTU Energy Conversion = Department of Energy Conversion and Storage**

- **Sustainable technologies for energy conversion and storage**
- **Located on two campuses near Copenhagen, Denmark: Lyngby and Risø**
- **230+ employees**
- **Our research span from fundamental investigations to component manufacture**
- **Focus on industrial collaboration and industrially relevant processes**
- **Created 2012, ringing together research groups from**
  - **Risø DTU National Laboratory for Sustainable Energy**
  - **DTU Chemistry**



# Introduction II

- **Extensive Solid oxide electrolysis and fuel cells (SOCs) research during the latest 2 – 3 decades**
- **Electrode kinetics have been studied intensively as the understanding of the kinetics is believed to be the key to major improvements of the SOC technology**
- **Several possible electrode mechanisms have been proposed and discussed together with the current density (cd) – overvoltage characteristics, and the area have been reviewed in many papers**
- **In spite of this there are serious disagreements about how the measured cd – overvoltage ( $i - V$ ) curves should be interpreted and modeled. As an important example, many (most?) authors – both experimentalists and modelers – continue to assume that a Butler –Volmer type equation describes the full  $i$ - $V$  curve well in spite of no direct experimental support for this hypothesis**

## Introduction III

**“The observation of Tafel behavior at moderate to high polarization states does not imply a charge-transfer-limited reaction at the solid/solid interface.**

**Reactions limited by gas-exposed surface chemistry and/or transport from the surface to the solid/solid interface often mimic Butler–Volmer response.**

**Furthermore, since surface processes are often activated, and can have similar partial-pressure dependencies as interfacial charge transfer, validation of Butler–Volmer parameters (extracted empirically from  $i$ – $V$  data) based on these criteria is insufficient to confirm/deny domination by interfacial charge transfer.”**

Quote from: S. Adler, W.G. Bessler, “Elementary kinetic modeling of solid oxide fuel cell electrode reactions” Chapter 29 in *Handbook of Fuel Cells - Fundamentals, Technology and Applications*, W. Vielstich, H. Yokokawa, and H. A. Gasteiger, Eds., Vol. 5, p. 441, John Wiley & Sons Ltd, Chichester (2009).



# $i - \eta$ relations for composite electrodes

- As current density ( $i$ ) vs. overvoltage ( $\eta$ ) results for composite electrodes are often interpreted using the Butler-Volmer equation (or similar exponential relations), let us see how it will look like if we assume B-V equation valid for the Ni-YSZ interface in a composite electrode like a Ni-YSZ cermet obeys B-V in the single TPB
- The equation:

$$i = i_0 \cdot \left\{ \exp \left[ \frac{\alpha_a F \eta}{RT} \right] - \exp \left[ -\frac{\alpha_c F \eta}{RT} \right] \right\}$$

exchange c.d.  $i_0$ , symmetry factors  $\alpha_r$  and overpotential  $\eta$ . It describes charge transfer across a single well-defined barrier

- We assume that porous electrode theory is valid for composite electrodes

# Porous electrodes with Butler-Volmer kinetics

## DC response of porous electrodes with the Butler-Volmer equation incorporated:

An analytic solution has been derived for the semi-infinite case:

$$I = 4\pi r \sqrt{\frac{r j_0}{\rho_s b}} \sinh\left(\frac{b\eta}{2}\right)$$

**r**= radius of electrolyte particle  
**j<sub>0</sub>**=exchange current density from the Butler-Volmer equation  
**ρ<sub>s</sub>**=resistivity of the electrolyte  
**b**=αnF/RT

F. A. Posey, J. Electrochem. Soc. 111 (1964) 1173.

A. Winsel, Z. Elektrochem. 66 (1962) 331.

A. Lasia, J. Electroanal. Chem. 397 (1995) 27.

# Linearity of electrodes with Butler-Volmer kinetics



## Butler-Volmer

## Porous electrode with Butler-Volmer

Equations:

$$j = j_0 \left[ e^{\frac{(1-\alpha)nF}{RT}\eta} - e^{\frac{-\alpha nF}{RT}\eta} \right]$$

Taylor expansion:

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

Criteria for linearity:

The linear term should be larger than the non-linear term giving:

$$\begin{aligned} & \Downarrow \\ & x > \frac{x^2}{2!} \\ & \Downarrow \\ & 2 > x = \frac{(1-\alpha)nF\eta}{RT} \\ & \Downarrow \\ & \eta < \frac{2RT}{(1-\alpha)nF} \end{aligned}$$

Equations:

$$I = 4\pi r \sqrt{\frac{rj_0}{\rho_s b}} \sinh\left(\frac{b\eta}{2}\right)$$

Taylor expansion:

$$\sinh(x) = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \dots$$

Criteria for linearity:

The linear term should be larger than the non-linear term giving:

$$\begin{aligned} & \Downarrow \\ & x > \frac{x^3}{3!} \\ & \Downarrow \\ & 6 > x^2 = \left(\frac{\alpha nF\eta}{2RT}\right)^2 \\ & \Downarrow \\ & \eta < \sqrt{6} \left(\frac{2RT}{\alpha nF}\right) \end{aligned}$$

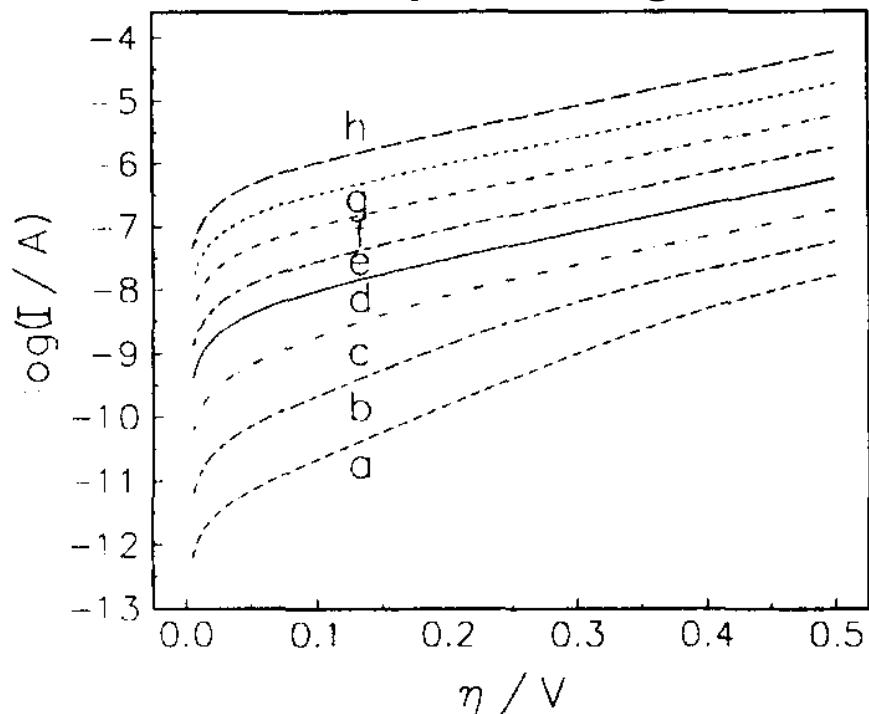
**Conclusion: The response of porous electrodes is a factor 2.45 “more linear” than simple B-V**

# Porous electrodes with Butler-Volmer kinetics

A. Lasia has calculated impedance spectra with the Butler-Volmer equation incorporated by a numerical approach.

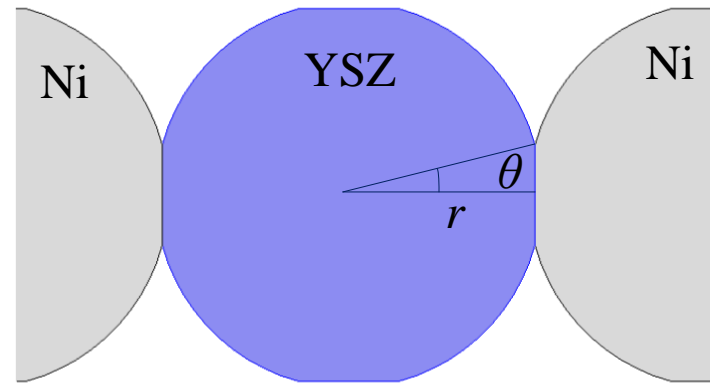
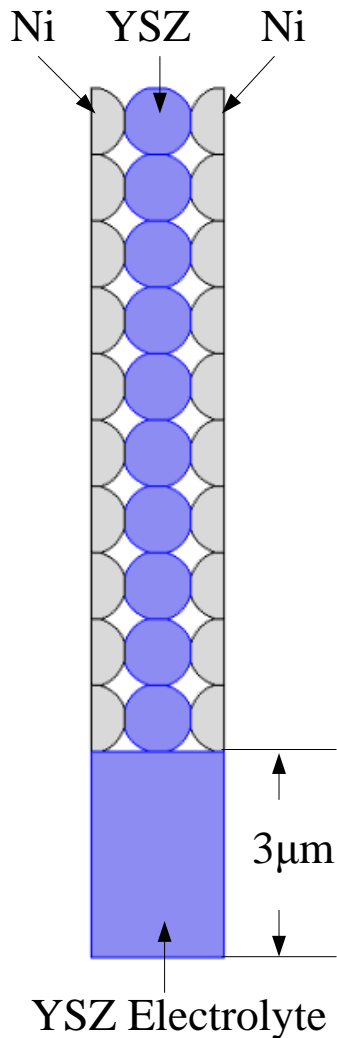
A. Lasia, J. Electroanal. Chem. 397 (1995) 27:

Tafel slope is changed



Tafel plots for the pore characterized by  $l = 0.05$  cm,  $r = 10^{-4}$  cm,  $\rho = 10$   $\Omega$  cm and ( $\alpha = 0.5$ : Exchange current densities  $j_0$  /A cm<sup>-2</sup>: (a)  $10^{-7}$ , (b)  $10^{-6}$ , (c)  $10^{-5}$ , (d)  $10^{-4}$ , (e)  $10^{-3}$ , (f)  $10^{-2}$ , (g)  $10^{-1}$  and (h) 1.

# Geometry



$$\theta=15^{\circ} \quad r=0.5\mu\text{m}$$

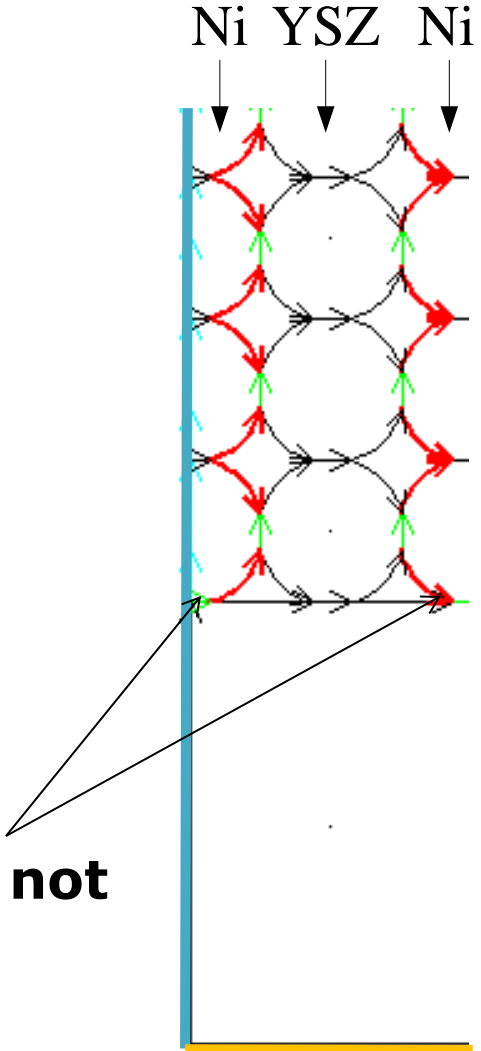
$$i = -\sigma \nabla V$$

$$\nabla \cdot (-\sigma \nabla V) = 0$$

T	1000°C
$\sigma_{\text{YSZ}}$	$3.34\text{e}4 \cdot \exp(-10300/T) = 10.24$ $(1/(\Omega \text{ m})) = 0.102 \text{ (S/cm)}$
$\sigma_{\text{Ni}}$	$3.27\text{e}6 - 1063.5 \cdot T = 1.92\text{e}6 \text{ (1/(\Omega m))}$ $= 1.92\text{e}-4 \text{ (S/cm)}$

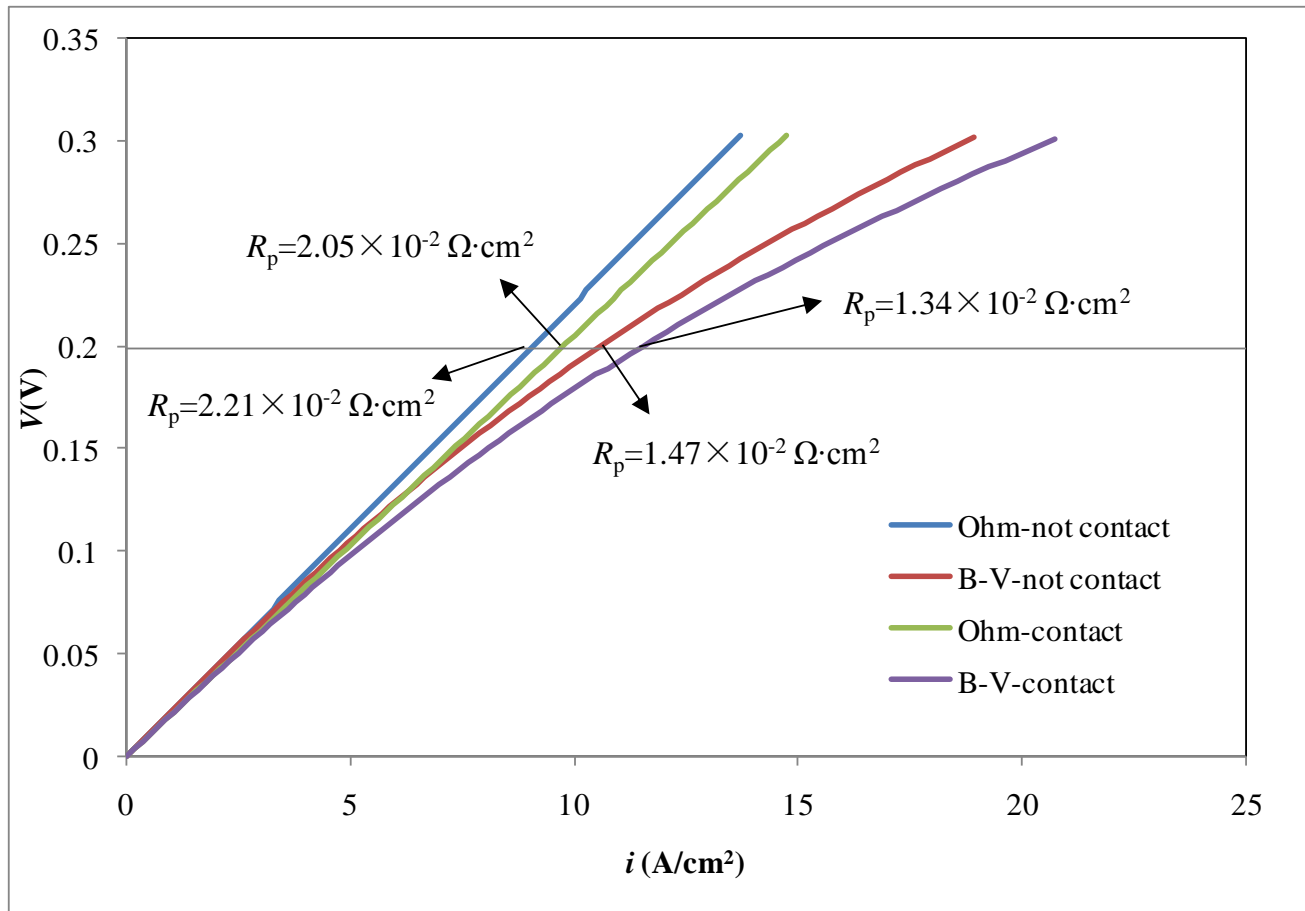
# Boundary condition

- Set the proton voltage on the surface of Ni  
(The red curves in the right figure)
- Set the boundary  $V_0 = 0$  (V)  
(The blue curves in the right figure)  
Symmetry
- Set the proton voltage on the outside surface of electrolyte  
(The orange line in the right figure)

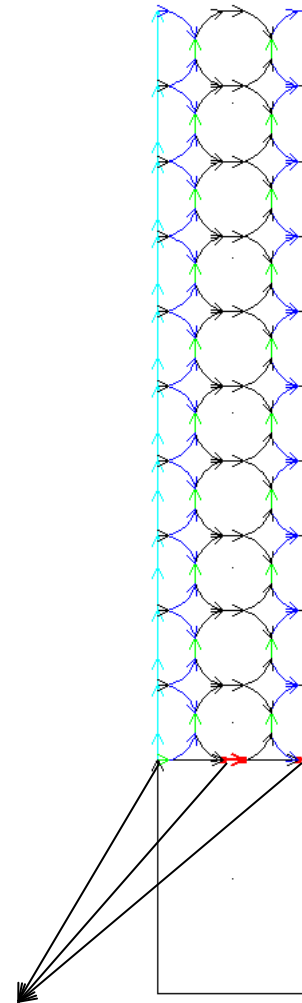

  
 $-V_{\text{tot}}$ 
  
 A given value

**Contact or not  
contact on  
electrolyte**

# Results—i-V curves



**This also shows why it is experimentally difficult to decide the form of the i-V**



**Average value of  $I$  or  $V$  at both Ni and YSZ particle boundaries**

# Experimental observations

- The performance results for solid oxide cells (SOC) reported in the literature are “all over the place”.
- Absolute values varies tremendously:
- Current density – voltage (i–V) curves more 10 times in values and also varies in shape
- Activation energies of both anodes and cathodes more than 2 times (3-4 for some); Ni-YSZ from 0.5 eV to 1.8 eV; O<sub>2</sub> LSM from 1.1 – 2.2 eV
- Degradation rates very different and failure modes very different
- Why?
- Different workers are obviously studying substantially different Ni-YSZ-electrodes even though they are intended to be identical



# YSZ electrolyte surface

Surface

Impurity layer	~ 0.5 nm
Layer enriched in $Y_2O_3$	~ 5 - 10 nm
Bulk phase YSZ	
a)	

Surface

Impurity layer	~ 0.5 nm
Layer enriched in $Y_2O_3$	~ 1 nm
Layer depleted in $Y_2O_3$	~ 5 nm
Bulk phase YSZ	
b)	

**YSZ with glassy surface layers of compositions of  $SiO_2$ ,  $Na_2O$ ,  $CaO$  +++.**

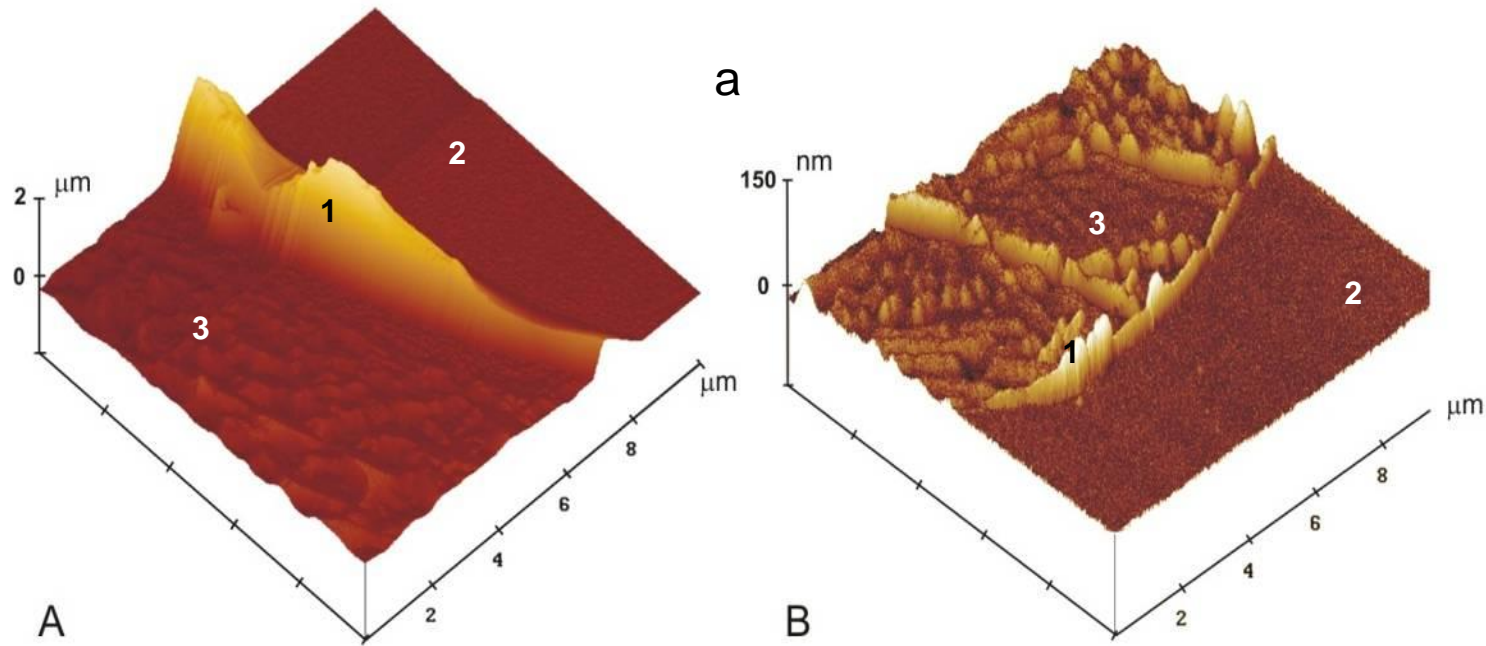
**a) Near equilibrium ( $> 1200\text{ }^{\circ}C$ ) for several hours.**

**b) Not near equilibrium - the original surface removed + short time (1 h) at  $500\text{ }^{\circ}C$ .**

**The exact YSZ surface depend on initial composition and on sample history**

**Similar segregations on perovskite surfaces, i.e. ceramic electrodes – for instance Sr enrichment on LSM and LSCo surfaces**

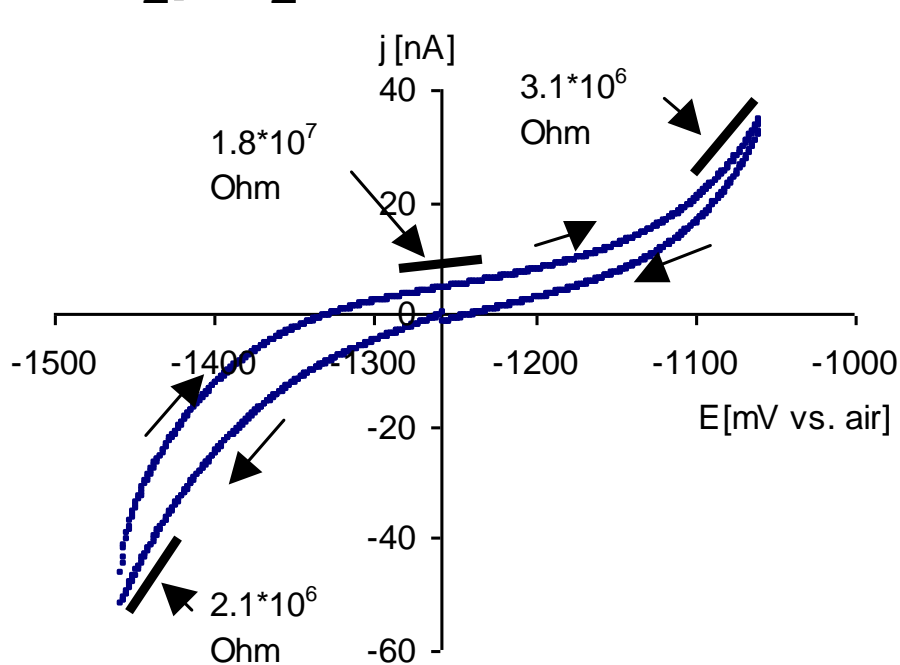
# Effects of materials impurity



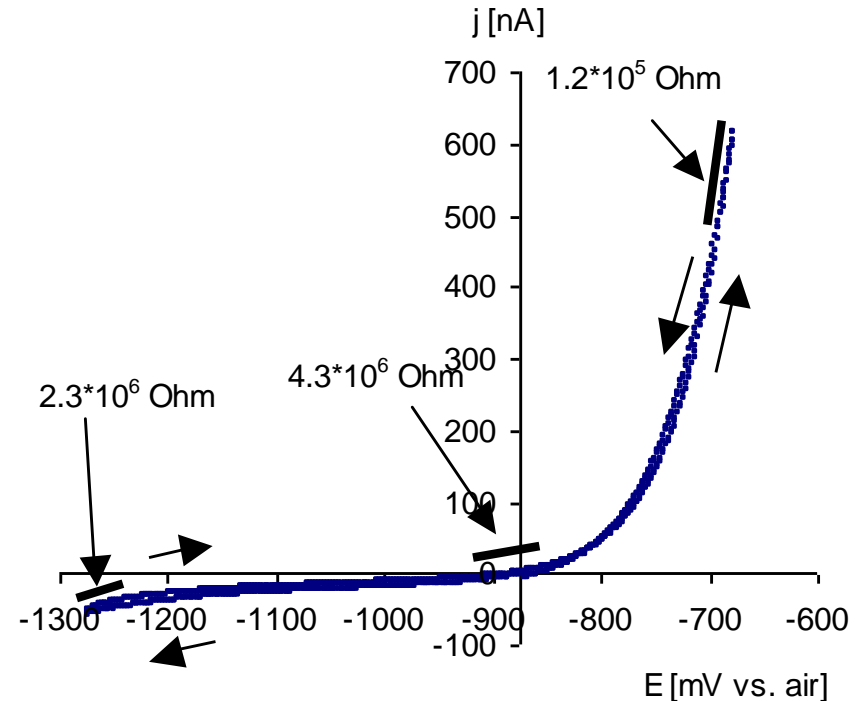
**Atomic force microscope pictures of: rim ridge (1) of impurity phases at TPB of Ni point electrodes on a YSZ after ca. 1 week test and removal Ni. A. “Impure” Ni = 99.8% Ni. B. “Pure” Ni = 99.99% Ni. (2) the YSZ surface exposed to the H<sub>2</sub>, and (3) the YSZ side of the YSZ-Ni. After K.V. Hansen, J. Electrochem. Soc., 151 (2004) A1436**

# Ni Point Electrode i-V curves

## H<sub>2</sub>/H<sub>2</sub>O



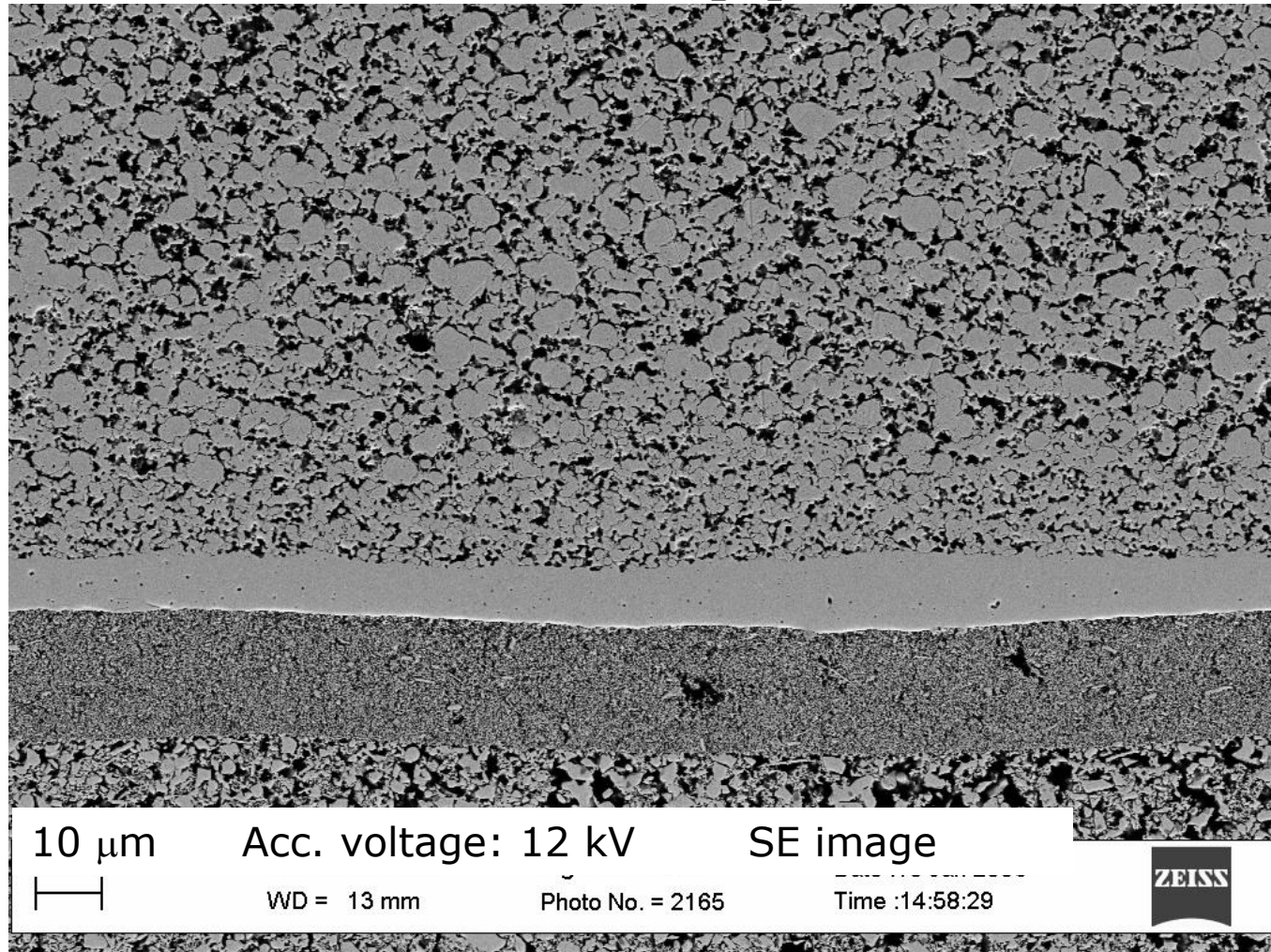
**Potential sweep (5 mV/s) at  
700° C, H<sub>2</sub> = 99.9%, H<sub>2</sub>O =  
0.1%,  $\mathcal{E}_0$  = -1259 mV vs. air**



**Potential sweep (5 mV/s) at  
700° C, H<sub>2</sub> = 2%, H<sub>2</sub>O = 19.7%,  
 $\mathcal{E}_0$  = -876 mV vs. air**

J. Høgh, K.V. Hansen and M. Mogensen, in *Proc. 26th Risø Internat. Symp. Mat. Science*, S. Linderroth et al., Editors, p. 235, Risø National Laboratory, Roskilde, Denmark (2005) .

# Ni-YSZ supported cell



**Ni/YSZ support**

**Ni/YSZ electrode**

**YSZ electrolyte**

**LSM-YSZ electrode**

10 μm

Acc. voltage: 12 kV

SE image



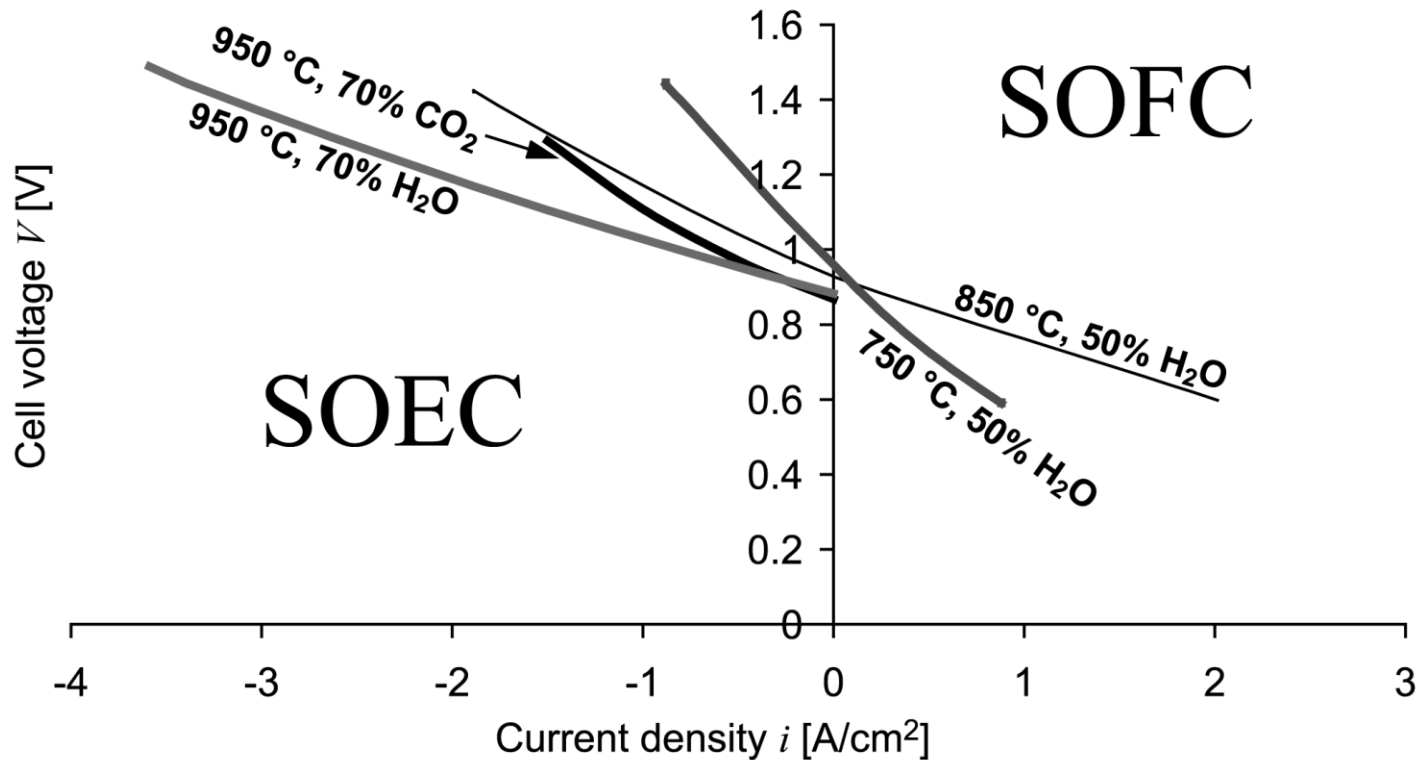
WD = 13 mm

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Time :14:58:29



# SOE/FC Cell Reversible Performance

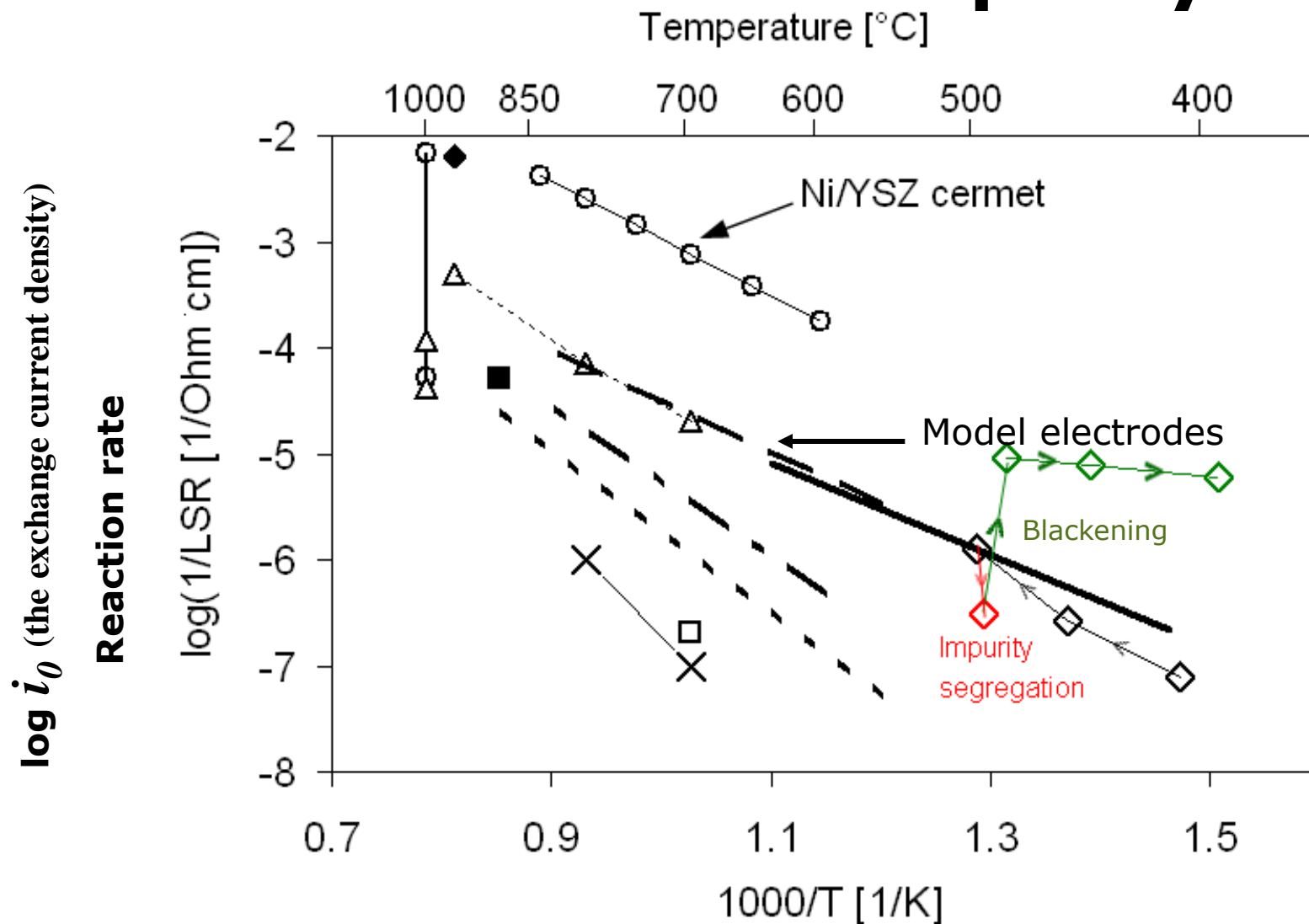


**$i - V$  curves for a Ni-YSZ-supported Ni/YSZ/LSM SOC: electrolyzer (negative current density) and fuel cell (positive current density) at different temperatures and steam or CO<sub>2</sub> partial pressures - balance is H<sub>2</sub> or CO.**

S.H. Jensen, P.H. Larsen, M. Mogensen, International Journal of Hydrogen Energy, 32 (2007) 3253

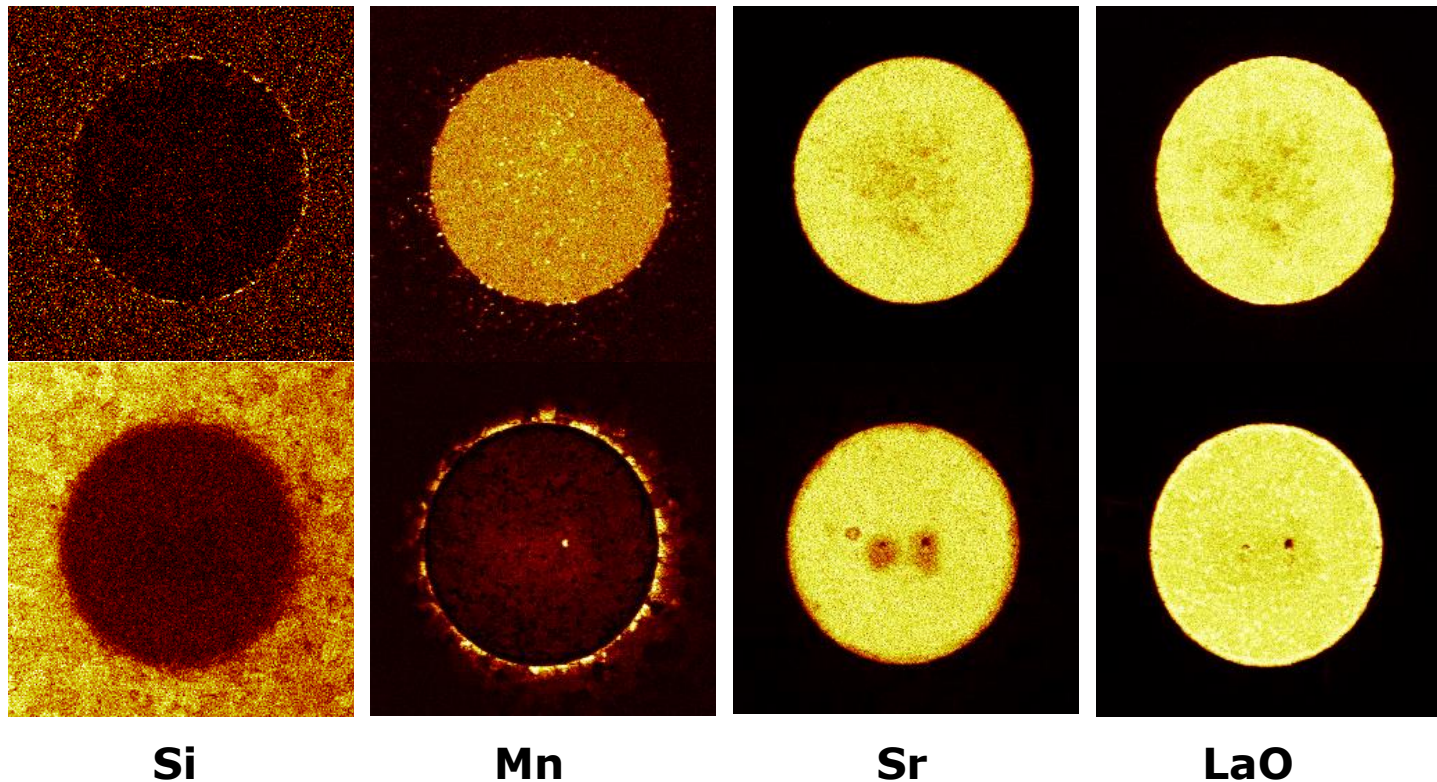


# Effect of materials impurity



Courtesy of Dr. Jens Høgh, DTU

# Surface composition



TOF-SIMS of two 100  $\mu\text{m}$  microelectrodes, a not tested reference (upper row) and an electrochemical tested (lower row) for the 4 signals from Si, Mn, Sr and LaO. The lighter, the higher is the signal (the counts) of a given species

# Arguments against Butler-Volmer relation being descriptive of the full i-V curve of SOC electrodes

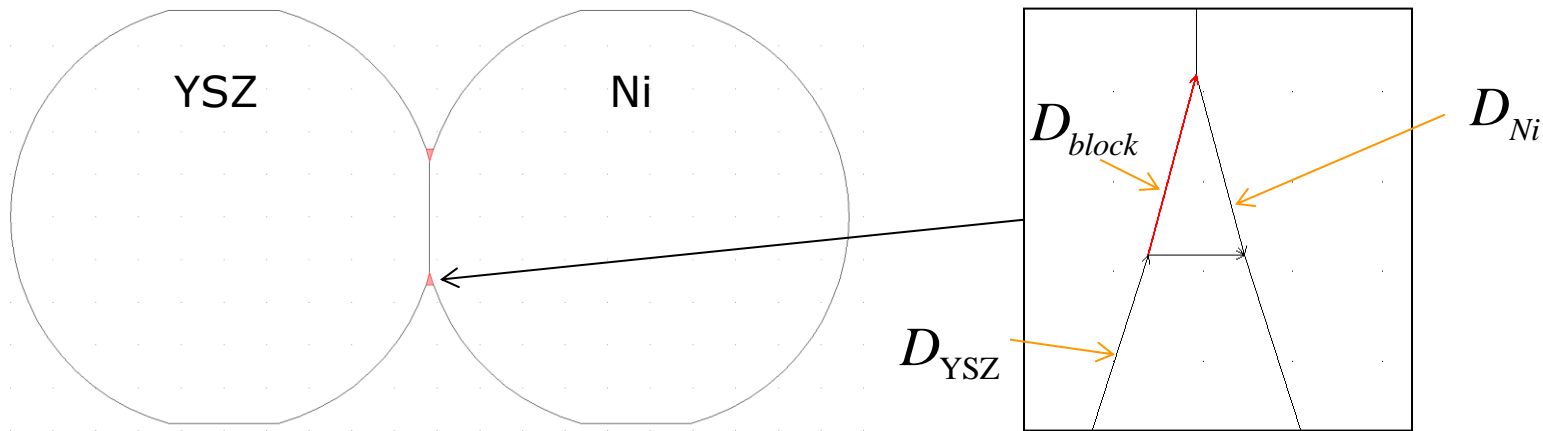
1. There will not be any single simple potential barrier to charge transfer: valid for all SOC electrodes including simple model electrode. The segregated surface layers and several types of surface sites make the charge transfer (ion transfer) limited by surface diffusion and transport through the surface layers
2. Electron transfer is across the non-controlled interface
3. Composite electrodes does not follow a Butler-Volmer expression
4. Complicated structures with several particle types involved will probably have a multistep reaction mechanisms with more than one process contributing to polarization resistance

**So, how to model instead?**



# Sketch of a model for proton diffusion in the YSZ - segregated phase interface being rate limiting

**Assumption: Segregations/impurity is only on the YSZ**



$$J = -D\nabla c, \nabla \cdot (-D\nabla c) = 0$$

D_Ni	$2.5e-3 \cdot \exp(-14650/R/T)$ $= 6.26e-4 \text{ (cm}^2/\text{s)} @ 1000^\circ\text{C}$
D_YSZ	$1.5 \cdot 10^{-6} \text{ (cm}^2/\text{s)} @ 1000^\circ\text{C}$
D_block	To be calculated from $R_p$

# Boundary condition

**There is a concentration drop between the 2 phases at TPB**

- Proton coverage at Ni surface

$$\theta_{Ni} = 0.23 \quad \Rightarrow \quad c_{Ni} = 5.98 \times 10^{-10} \text{ mol/cm}^2$$

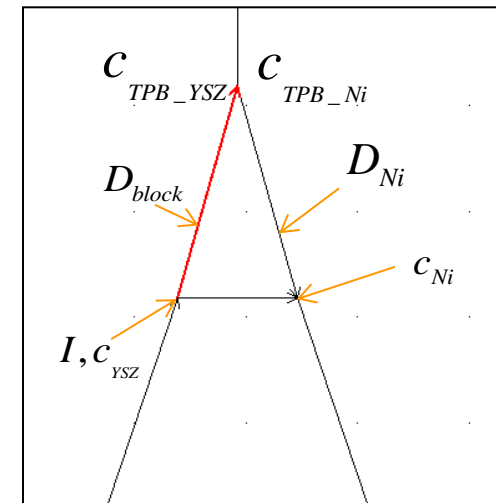
$$\Gamma = 2.6 \times 10^{-9} \text{ mol/cm}^2 \quad [2]$$

- Proton concentration at TPB in YSZ

$$c_{YSZ,TPB} = c_{YSZ,0} \frac{p_{H_2O}}{p_{H_2O,0}}$$

$$E = E_0 + \frac{RT}{2F} \ln \left( \frac{p_{H_2O}}{p_{H_2} \sqrt{p_{O_2}}} \right)$$

$$E_0 = \frac{\Delta G}{2F} = 0.920V @ 1000^\circ C$$



# Proton concentration at TPB in YSZ

## Assumption:

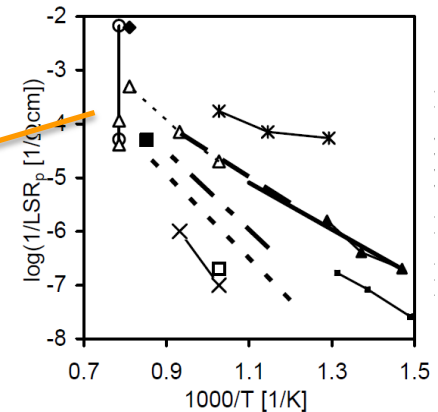
1. The chemical potential difference of  $H^+$  across the TPB is the same as in the bulk across Ni-YSZ interface, which is known from literature
2. The density of adsorption sites,  $\Gamma$ , on Ni and YSZ surfaces is the same (not necessarily correct)

$$\Delta\mu = RT \ln \frac{c_{YSZ,0}(\text{mol/cm}^3)}{c_{Ni,0}(\text{mol/cm}^3)} = RT \ln \frac{c_{YSZ,0}(\text{mol/cm}^2)}{c_{Ni,0}(\text{mol/cm}^2)} = RT \ln \frac{\theta_{YSZ,0}}{\theta_{Ni,0}}$$

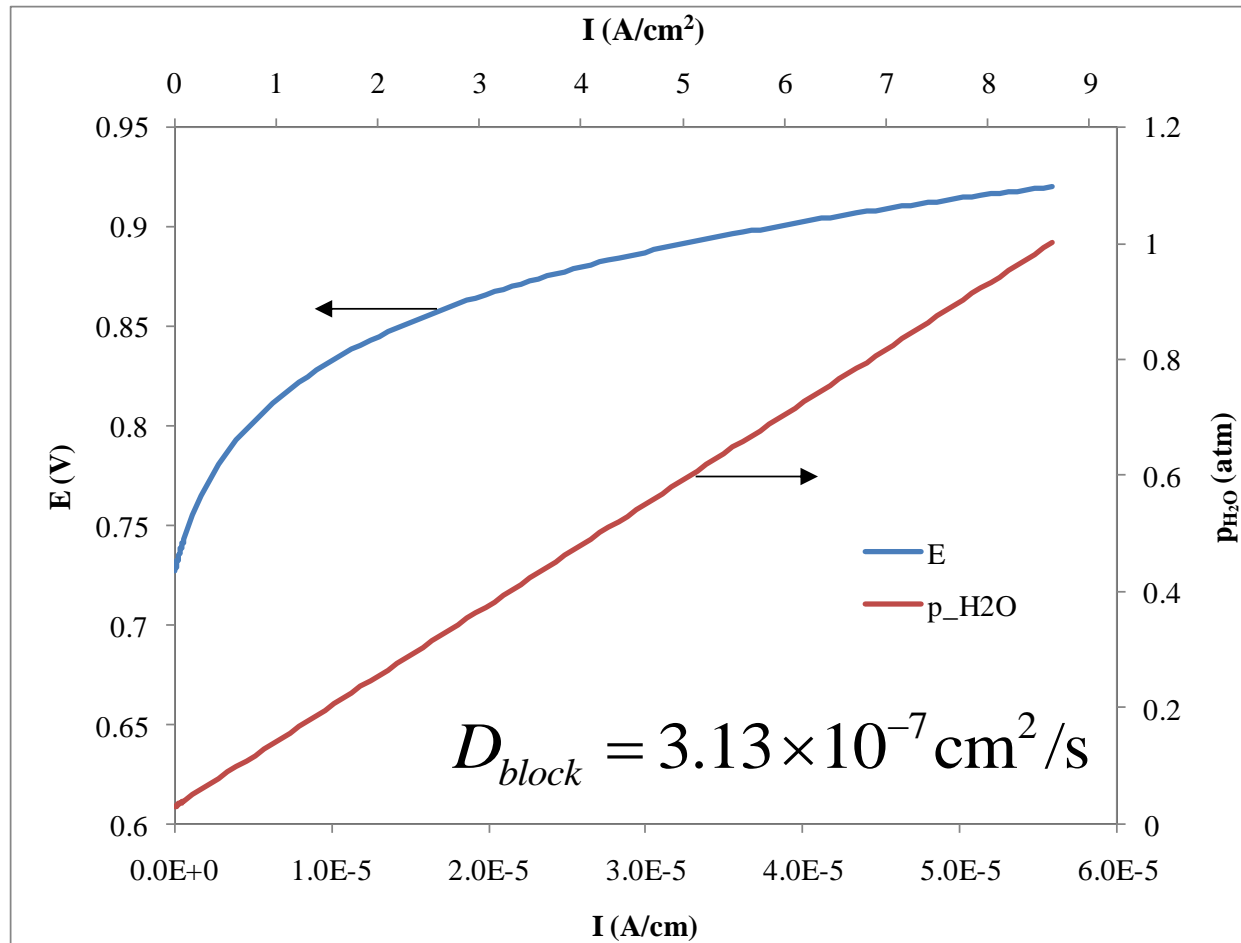
➔  $c_{YSZ,0} = 2.07 \times 10^{-3} \cdot \Gamma = 5.382 \times 10^{-12} \text{ mol/cm}^2$

- Resistance at OCV

$$LSR_p = dE / dI = 3.16 \times 10^4 \text{ } \Omega \times \text{cm}$$



# Results—i-V curves



$$I(\text{A/cm}^2) = I(\text{A/cm}) \frac{2\pi r \sin \theta}{\pi (r \sin \theta)^2}$$

# Concluding remarks

- **Butler-Volmer not feasible to describe SOC electrode kinetics**
- **SOC interfaces are very sensitive to history in general and thermal history in particular – poor reproducibility - difficult to make identical cells in different institutes /companies**
- **Thus, searching for one universal rate limiting reaction step for a given type of SOC composite electrode may not be very useful**
- **Instead the study of which TPB structures and of which physical and chemical properties of solids that give best electrocatalytic activity– like in Joachim Maier’s example with perovskites yesterday - is recommended**
- **Furthermore, better three-dimensional micro-models describing charge transport to and from the electrodes are needed**
- **Descriptions/modeling of specific SOC electrodes may be very useful if benchmarked against experimental data from the same electrode**
- **The wise strategy is to gain insight through understanding many examples as deep as possible**

# Acknowledgement

## We acknowledge

- Support from our sponsors
- Danish Energy Authority  DANISH ENERGY AUTHORITY
- Energinet.dk 
- EU 
- Topsoe Fuel Cell A/S  *clean, efficient and reliable*
- Danish Programme Committee for Sustainable Energy and Environment
- The work of many colleagues over the years

# Thank you for your attention!